

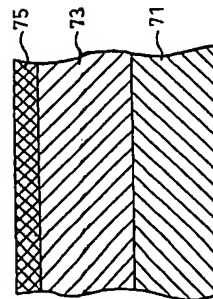
(21) Application No 0023929.3	(51) INT CL ⁷ F01N 3/28, B01D 53/94
(22) Date of Filing 15.09.1999	(52) UK CL (Edition S) B1W WAX W10C W10D W17A W18D W5A W6A W6R W6X W7J W9P
Date Lodged 28.09.2000	(56) Documents Cited EP 0885657 A2 WO 97/23278 A1 US 5473887 A
(30) Priority Data (31) 10264596 (32) 18.09.1998 (33) JP (31) 11220418 (32) 03.08.1999	(58) Field of Search UK CL (Edition S) B1W WAX WD WX INT CL ⁷ F01N 3/08 3/10 3/18 3/20 3/24 3/28 3/36 ONLINE: EPDOC, JAPID, WPI
(62) Divided from Application No 8921839.8 under Section 15(4) of the Patents Act 1977	
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(54) Abstract Title
An exhaust gas purification device for an internal combustion engine

(57) A converter containing a NOx absorbing and reducing catalyst 73 is disposed in the exhaust passage of an internal combustion engine. The upstream half portion (portion of the inlet side) of the substrate 71 of the NOx absorbing and reducing catalyst 73 in the converter carries the oxygen storage component 75 that absorbs oxygen in the exhaust gas when the air-fuel ratio of the exhaust gas is lean and releases the absorbed oxygen when the air-fuel ratio of the exhaust gas flowing in is rich in addition to carrying the NOx absorbing and reducing catalyst 73. After NOx is absorbed by the NOx absorbing and reducing catalyst 73 as a result of operating the engine at a lean air-fuel ratio, the engine is operated at a rich air-fuel ratio, so that NOx is released from the NOx absorbing and reducing catalyst 73 and is purified by reduction. Here, oxygen is released from the oxygen storage component 75 carried by the substrate 71 and is reacted with the H₂ and CO components in the exhaust gas, so that the temperature of the NOx absorbing and reducing catalyst 73 is raised within short periods of time due to the heat of reaction. Therefore, the catalyst exhibits increased activity and the NOx absorbing and reducing catalyst 73 exhibits improved NOx purification capability. The oxygen storage component 75 is ceria-zirconia solid solution and also works as a SOx trap.

Fig. 3

EXHAUST
GAS →



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Fig. 1

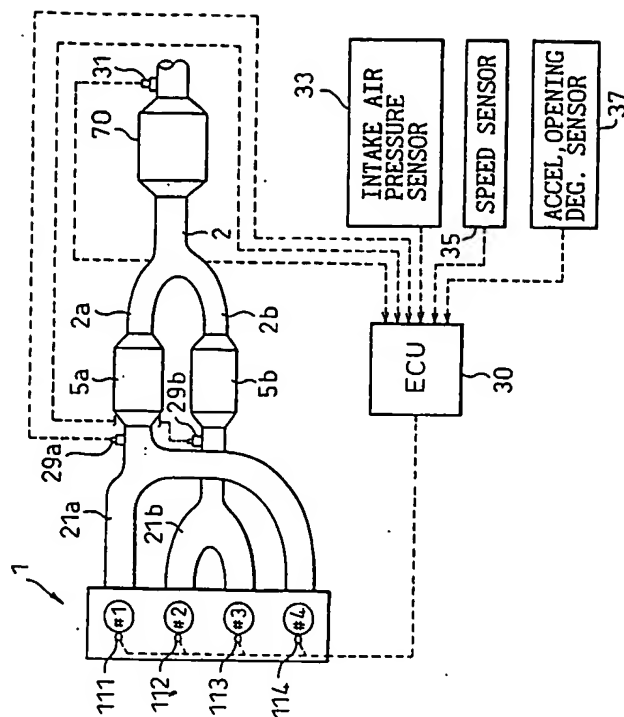


Fig. 2

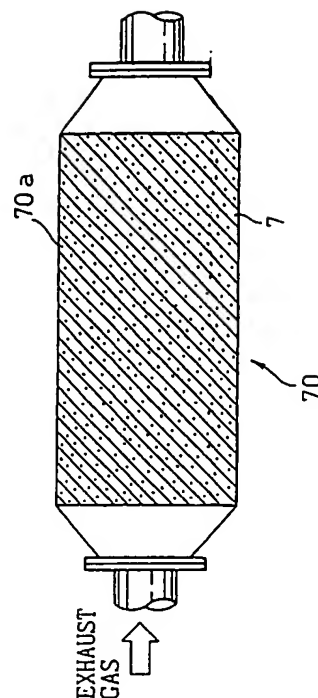


Fig. 3

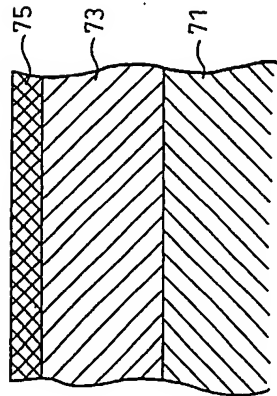
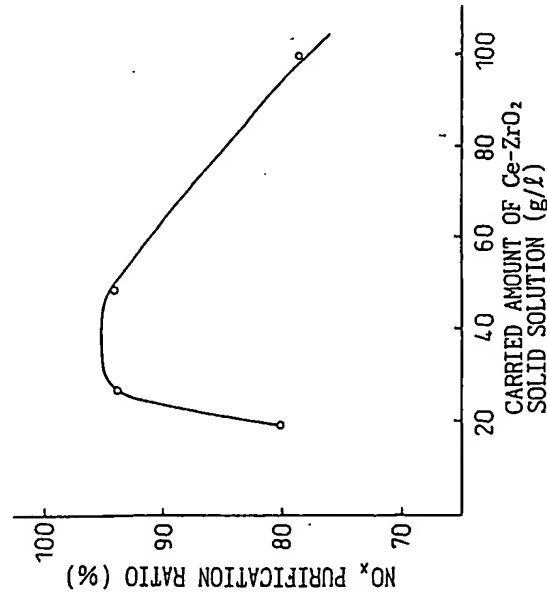
EXHAUST
GAS →

Fig. 4



5 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an exhaust gas purification device for an internal combustion engine.

More specifically, the invention relates to an exhaust gas purification device equipped with a NOx absorbing and reducing catalyst which absorbs NOx in the exhaust gas when the air-fuel ratio of the exhaust gas flowing in is lean, and releases and purifies by reduction the absorbed NOx when the air-fuel ratio of the exhaust gas flowing in is rich.

2. Description of the Related Art

There has been known a NOx absorbing and reducing catalyst which absorbs NOx (nitrogen oxides) in the exhaust gas when the air-fuel ratio of the exhaust gas flowing in is lean, and releases and purifies, by reduction, the absorbed NOx when the air-fuel ratio of the exhaust gas flowing in becomes rich.

An exhaust gas purification device using the NOx absorbing and reducing catalyst of this type has been disclosed in, for example, Japanese Patent No. 2600492.

In the exhaust gas purification device of the above patent, the NOx absorbing and reducing catalyst is disposed in the exhaust passage of an engine that operates at a lean air-fuel ratio. During a lean air-fuel ratio operation of the engine, NOx in the exhaust gas is absorbed by the NOx absorbing and reducing catalyst. When NOx is absorbed in an increased amount by the NOx absorbing and reducing catalyst, the rich spike operation is executed to operate the engine at an air-fuel ratio (or rich air-fuel ratio) smaller than the stoichiometric air-fuel ratio for a short period of time. Thus, the NOx that is absorbed is released from the NOx

absorbing and reducing catalyst, and the released NOx is purified by reduction. That is, when the engine operating air-fuel ratio becomes rich, the oxygen concentration in the exhaust gas sharply drops compared with when the engine is operated at a lean air-fuel ratio, and the amounts of unburned HC and CO components sharply increase in the exhaust gas. Therefore, when the operating air-fuel ratio is changed over to a rich air-fuel ratio by the rich spike operation, NOx is released from the NOx absorbing and reducing catalyst and is reduced by being reacted with the unburned HC and CO components in the exhaust gas on the NOx absorbing and reducing catalyst.

The above-mentioned Japanese Patent No. 2600492 further discloses a constitution for purifying the HC and CO components emitted from the engine at the start of the engine by disposing a three-way catalyst in the exhaust passage on the upstream side of the NOx absorbing and reducing catalyst. The three-way catalyst of the above patent is disposed near the engine exhaust manifold through which the exhaust gas of a high temperature from the engine passes, and is heated to the activated temperature within a short period of time after the start of the engine. Therefore, HC and CO emitted in relatively large amounts from the engine are oxidized by the three-way catalyst after the engine started, and the quality of the exhaust gas, before the engine is warmed-up, is improved.

With the three-way catalyst being disposed in the exhaust passage on the upstream side of the NOx absorbing and reducing catalyst as taught in the above-mentioned Japanese Patent No. 2600492, it was considered that the ability of the NOx absorbing and reducing catalyst for purifying the exhaust gas often drops when the three-way catalyst possesses an O₂ storage capability due to a delay in the change of the air-fuel ratio of the exhaust gas flowing into the NOx absorbing and reducing

catalyst.

As is widely known, the three-way catalyst carries, as an additive, a metal component such as cerium Ce in addition to noble metal catalyst components such as platinum Pt, palladium Pd and rhodium Rh, so as to exhibit the O₂ storage capability. That is, cerium carried as an additive by the catalyst bonds to oxygen in the exhaust gas when the air-fuel ratio of the exhaust gas flowing into the catalyst is higher than the stoichiometric air-fuel ratio (when the air-fuel ratio of the exhaust gas is lean) to form ceria (cerium oxide IV: CeO₂) which stores oxygen. Further, when the air-fuel ratio of the exhaust gas flowing in is smaller than the stoichiometric air-fuel ratio (when the air-fuel ratio of the exhaust gas is rich), ceria releases oxygen and is transformed into cerium oxide III (Ce₂O₃); i.e., oxygen is released. Thus, the three-way catalyst having an O₂ storage capability releases oxygen when the air-fuel ratio of the exhaust gas changes from the lean side to the rich side, and the air-fuel ratio of the exhaust gas that has passed through the three-way catalyst is maintained to be close to the stoichiometric air-fuel ratio, as long as oxygen is released from the three-way catalyst, even when the air-fuel ratio of the exhaust gas flowing into the three-way catalyst has changed to the rich side.

However, when the three-way catalyst disposed in the exhaust passage on the upstream side of the NOx absorbing and reducing catalyst possesses an O₂ storage capability, the exhaust gas flowing into the NOx absorbing and reducing catalyst does not readily acquire a rich air-fuel ratio but is temporarily maintained near the stoichiometric air-fuel ratio even when the air-fuel ratio of the exhaust gas from the engine has changed from the lean side to the rich side due to the rich spike operation of the engine. When the air-fuel ratio of the exhaust gas is changed from a lean air-fuel ratio to an

air-fuel ratio close to the stoichiometric air-fuel ratio, NOx is released from the NOx absorbing and reducing catalyst. However, in this case, the air-fuel ratio of the exhaust gas is not rich enough, i.e., the exhaust gas is not containing HC and CO components in amounts sufficient for reducing all of NOx released and, hence, NOx that has not been reduced flows out to the downstream side of the NOx absorbing and reducing catalyst.

10: When the NOx absorbing and reducing catalyst was used, therefore, it was not considered desirable to dispose the three-way catalyst having an O₂ storage capability in the exhaust passage on the upstream side of the NOx absorbing and reducing catalyst. When the three-way catalyst was disposed in the exhaust passage on the upstream side, therefore, it was considered that some countermeasure is required, for example, to remove cerium from the three-way catalyst, in order to lower the O₂ storage capability.

20 According to the study conducted by the present inventors, however, it was found that when NOx is to be released from the NOx absorbing and reducing catalyst, the NOx absorbing and reducing catalyst exhibits enhanced performance for purifying NOx when the three-way catalyst or the like catalyst having O₂ storage components is disposed at a position close to the NOx absorbing and reducing catalyst on the upstream side thereof. That is, when NOx is to be released from the NOx absorbing and reducing catalyst, the exhaust gas flowing into the catalyst must have a rich air-fuel ratio. In this case, when oxygen is released from the O₂ storage components disposed at a position close to the NOx absorbing and reducing catalyst on the upstream side thereof, it has been found that NOx is released and reduced at a greatly increased rate.

35 It has not been clarified yet why the catalyst having O₂ storage components disposed near the NOx

absorbing and reducing catalyst on the upstream side thereof helps improve the performance of the NOx absorbing and reducing catalyst for purifying the exhaust gas. However, one of the causes is considered to be that, if the O₂ storage components exist at a position close to the upstream side of the NOx absorbing and reducing catalyst when the exhaust gas of a rich air-fuel ratio is supplied, the HC and CO components in the exhaust gas are oxidized by the oxygen released from the O₂ storage components and the temperature of the catalyst components on the NOx absorbing and reducing catalyst rises due to the heat of reaction. That is, one of the reasons is attributed to the release of NOx from the NOx absorbing and reducing catalyst promoted by the rise of temperature of the NOx absorbing and reducing catalyst components, whereby the catalytic activity is improved to improve the NOx purification ratio. Though this point will be described later in detail, there arises a problem in that the purifying performance of the NOx absorbing and reducing catalyst often cannot be utilized to a sufficient degree, contrary to the conventional opinion, if the O₂ storage capability is eliminated as much as possible from the three-way catalyst or the like catalyst disposed on the upstream side of the NOx absorbing and reducing catalyst.

When the exhaust gas is rendered to possess a rich air-fuel ratio by executing the rich spike operation during the lean air-fuel ratio operation as taught in the above-mentioned Japanese Patent No. 2600492, the amounts of HC and CO components in the exhaust gas increase sharply. However, the HC and CO components tend to adhere on the catalyst components on the NOx absorbing and reducing catalyst. When the amounts of HC and CO components sharply increase in the exhaust gas flowing into the NOx absorbing and reducing catalyst, therefore, the surfaces of the catalyst components are covered with HC and CO. Therefore, the catalytic function drops,

i.e., HC contamination and CO contamination take place, and the NOx absorbing and reducing catalyst exhibits decreased ability for purifying NOx.

SUMMARY OF THE INVENTION

The object of the present invention is to provide an exhaust gas purification device for an internal combustion engine capable of exhibiting a high NOx conversion capability by solving one or more of the above-mentioned problems.

According to the present invention, there is provided an exhaust gas purification device for an internal combustion engine comprising a NOx absorbing and reducing catalyst which absorbs NOx in the exhaust gas when the air-fuel ratio of the exhaust gas flowing in is lean and releases the absorbed NOx and purifies it by reduction when the air-fuel ratio of the exhaust gas flowing in is rich disposed in an exhaust passage of the internal combustion engine which is capable of selecting, as required, the operation at a lean air-fuel ratio and the operation at a rich air-fuel ratio, so that the NOx absorbing and reducing catalyst absorbs NOx in the exhaust gas when the engine is operated at a lean air-fuel ratio and that the absorbed NOx is released from the NOx absorbing and reducing catalyst and is purified by reduction when the engine is operated at a rich air-fuel ratio;

wherein the NOx absorbing and reducing catalyst includes a substrate, a NOx absorbing and reducing

catalyst layer carrying NOx absorbing and reducing catalyst components on the substrate, and an oxygen storage component layer carrying oxygen storage components which absorb oxygen in the exhaust gas when the air-fuel ratio of the exhaust gas is lean and release the absorbed oxygen when the air-fuel ratio of the exhaust gas is rich, the oxygen storage component layer being formed on the NOx absorbing and reducing catalyst layer.

According to the invention, the NOx absorbing and reducing catalyst has a two-layer-coated structure including the NOx absorbing and reducing catalyst layer formed on the substrate, and the oxygen storage component layer formed on the upper side (i.e., on the exhaust side) of the NOx absorbing and reducing catalyst layer. When NOx is released from the NOx absorbing and reducing catalyst, therefore, heat produced by the reaction of CO and the like in the exhaust gas in the oxygen storage component layer is directly transmitted to the NOx absorbing and reducing catalyst components, whereby the temperature of the NOx absorbing and reducing catalyst components is efficiently raised.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood from the description as set forth hereinafter with reference to the accompanying drawings in which:

Fig. 1 is a view schematically illustrating an embodiment of the present invention when it is applied to an internal combustion engine for automobiles;

Fig. 2 is a sectional view illustrating the constitution of another embodiment of the converter of Fig. 1;

Fig. 3 is a view illustrating the constitution of the converter of Fig. 2 in detail; and

Fig. 4 is a view illustrating a change in the NOx purification ratio based on the amounts of the oxygen storage components that are carried.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, embodiments of the exhaust gas purification device according to the present invention will be explained with reference to the attached drawings.

Fig. 1 is a view schematically illustrating the constitution of an embodiment in which the present invention is applied to an internal combustion engine for automobiles.

In Fig. 1, reference numeral 1 denotes an internal combustion engine for automobiles. In this embodiment, the engine 1 is a four-cylinder gasoline engine having four cylinders #1 to #4 which are equipped with fuel injection valves 111 to 114 for injecting fuel directly into the cylinders. As will be described later, the internal combustion engine 1 of this embodiment is a lean burn engine, i.e., an engine capable of operating at a lean air-fuel ratio larger than a stoichiometric air-fuel ratio.

In this embodiment, the cylinders #1 to #4 are divided into two groups each including two cylinders for which the ignition timings do not occur consecutively (in the embodiment of Fig. 1, for example, the order of igniting the cylinders is 1-3-4-2, the cylinders #1 and #4 constituting a group, and the cylinders #2 and #3 constituting another group). Exhaust ports of the cylinders are connected to exhaust manifolds for each of

the cylinder groups, and are connected to exhaust passages for each of the cylinder groups. In Fig. 1, reference numeral 21a denotes an exhaust manifold for connecting the exhaust ports of the group of cylinders #1 and #4 to a separate exhaust passage 2a, and 21b denotes an exhaust manifold for connecting the exhaust ports of the group of cylinders #2 and #4 to another separate exhaust passage 2b. In this embodiment, start catalysts 5a and 5b comprising three-way catalysts are disposed in the separate exhaust passages 2a and 2b. The separate exhaust passages 2a and 2b meet together in a common exhaust passage 2 on the downstream side of the start catalysts.

In the common exhaust passage 2 is disposed a converter 70 having a NOx absorbing and reducing catalyst 7, that will be described later, contained in a casing. The constitution of the converter 70 will be described later.

In Fig. 1, reference numerals 29a and 29b denote upstream air-fuel ratio sensors disposed in the separate exhaust passages 2a and 2b on the upstream side of the start catalysts 5a and 5b, and reference numeral 31 denotes a downstream air-fuel ratio sensor disposed in the exhaust passage 2 on the downstream side of the converter 70. The air-fuel ratio sensors 29a, 29b and 31 are so-called linear air-fuel ratio sensors that produce voltage signals corresponding to the air-fuel ratios of the exhaust gas over a wide range of air-fuel ratios.

In Fig. 1, further, reference numeral 30 denotes an electronic control unit (ECU) for the engine 1. In this embodiment, the ECU 30 is a microcomputer of a known constitution including RAM, ROM and CPU, and executes basic control operations such as controlling the ignition timings for the engine 1 and controlling the fuel injection. In addition to executing the above-mentioned basic control operations, the ECU 30 in this embodiment executes the control operation to change the engine

operating air-fuel ratio by changing the fuel injection mode of the direct cylinder fuel injection valves 111 to 114 based on the engine operating conditions, as will be described later. In this embodiment, further, the ECU 30 estimates the amount of NOx absorbed in the NOx absorbing and reducing catalyst relying on the engine operating condition, by a method that will be described later, and executes the rich spike operation for changing the operating air-fuel ratio over to a rich air-fuel ratio for a short period of time during the lean air-fuel ratio operation of the engine to release the absorbed NOx when the estimated amount of NOx absorption has increased to a predetermined amount.

The input ports of the ECU 30 receive signals from the upstream air-fuel ratio sensors 29a and 29b representing the air-fuel ratios of the exhaust gas on the upstream side of the start catalysts 5a and 5b, receive a signal from the air-fuel ratio sensor 31 representing the air-fuel ratio of the exhaust gas on the downstream side of the converter 70, receive a signal corresponding to the intake air pressure of the engine from an intake air pressure sensor 33 disposed in the engine intake manifold that is not shown, and further receive a signal corresponding to the engine rotational speed from a rotational speed sensor 35 disposed near the engine crank shaft (not shown). In this embodiment, further, the ECU 30 receives through the input port a signal representing the amount the accelerator pedal is depressed by a driver (degree of accelerator opening) from an accelerator opening degree sensor 37 disposed near the accelerator pedal (not shown) of the engine. The output ports of the ECU 30 are connected to the fuel injection valves 111 to 114 of the cylinders through a fuel injection circuit that is not shown in order to control the amounts of fuel injection into the cylinders and the timings for fuel injection.

In this embodiment, the ECU 30 operates the engine 1

in one of the following five combustion modes based on the engine operating conditions:

- ① A lean air-fuel ratio stratified charge combustion (fuel is injected during the compression stroke of the cylinder);
 - ② A lean air-fuel ratio uniform mixture/stratified charge combustion (fuel is injected during the intake stroke and the compression stroke of the cylinder);
 - ③ A lean air-fuel ratio uniform mixture combustion (fuel is injected during the intake stroke of the cylinder);
 - ④ A stoichiometric air-fuel ratio uniform mixture combustion (fuel is injected during the intake stroke of the cylinder); and
 - ⑤ A rich air-fuel ratio uniform mixture combustion (fuel is injected during the intake stroke of the cylinder).
- In the light-load operating region of the engine 1, the lean air-fuel ratio uniform mixture combustion ① is effected. In this state, fuel is injected into the cylinder only one time in the latter half of the compression stroke of the cylinder, and the injected fuel forms a layer of the mixture of a combustible air-fuel ratio near the spark plug in the cylinder. In this operating condition, the fuel is injected in a very small amount, and the air-fuel ratio in the cylinder as a whole is from about 25 to about 30.

As the load increases from the state ① above to enter into the low-load operating region, the lean air-fuel ratio uniform mixture/stratified charge combustion ② is effected. The amount of fuel injected into the cylinder increases with an increase in the engine load. In the case of the stratified charge combustion ① in which fuel is injected in the latter half of the compression stroke, a limitation is imposed on the

injection time and, hence, a limitation is imposed on the amount of fuel that can be used for forming the stratified charge. In this load region, therefore, fuel is injected in the upstream half of the intake stroke in an amount to compensate for the lack of fuel injected in the latter half of the compression stroke, so that fuel is supplied in a target amount into the cylinder. Fuel injected into the cylinder in the upstream half of the intake stroke forms a very lean uniform mixture before being ignited. In the latter half of the compression stroke, fuel is further injected into this very lean and uniform mixture thereby to form a layer of the combustible mixture that can be ignited near the spark plug. At the time of ignition, the layer of the combustible mixture starts burning, and the flame propagates to the surrounding lean mixture layer to realize a stable combustion. In this state, the amount of fuel supplied by being injected in the intake stroke and in the compression stroke, becomes greater than the amount in the state ①, but the air-fuel ratio as a whole is still lean (e.g., about 20 to about 30 in terms of the air-fuel ratio).

As the engine load further increases, the engine 1 effects the lean air-fuel ratio uniform mixture combustion ②. In this state, the fuel is injected only one time in the upstream half of the intake stroke, and the amount of fuel injection becomes larger than that of ② above. The uniform mixture formed in the cylinder in this state assumes a lean air-fuel ratio (e.g., about 15 to 25 in terms of the air-fuel ratio) which is relatively close to the stoichiometric air-fuel ratio.

As the engine load further increases to enter into the high-load operating region of the engine, the amount of fuel is further increased from the state ③, and the stoichiometric air-fuel ratio uniform mixture operation ④ is effected. In this state, a uniform mixture of the stoichiometric air-fuel ratio is formed in the cylinder,

and the engine produces an increased output. As the engine load further increases to enter into the full-load operating region, the amount of fuel injection is further increased from the state ④, and the rich air-fuel ratio uniform mixture operation ⑤ is effected. In this state, the uniform mixture formed in the cylinder acquires a rich air-fuel ratio (e.g., about 12 to 14 in terms of the air-fuel ratio).

In this embodiment, optimum operation modes (① to ⑤) have been set in advance through experiment based on the degree of accelerator opening (amount the accelerator pedal is depressed by the driver) and the engine rotational speed, and have been stored in the ROM of ECU 30 as a map using the degree of accelerator opening and the engine rotational speed. While the engine 1 is in operation, the ECU 30 determines which operation mode must be selected out of the above-mentioned operation modes ① to ⑤ based on the degree of accelerator opening detected by the accelerator opening degree sensor 37 and the engine rotational speed, and determines the amount of fuel injection and the timing for fuel injection based on the mode.

When the mode (lean air-fuel ratio combustion) is selected out of ① to ⑤, the ECU 30 determines the amount of fuel injection from the degree of accelerator opening and the engine rotational speed based on the map prepared in advance for each of the modes ① to ⑤. When the mode (stoichiometric air-fuel ratio or rich air-fuel ratio uniform mixture combustion) is selected from ④ and ⑤, the ECU 30 determines the amount of fuel injection from the intake air pressure detected by the intake air pressure sensor 33 and the engine rotational speed based on the map prepared in advance for each of the modes ④ and ⑤.

When the mode ④ (stoichiometric air-fuel ratio uniform mixture combustion) is selected, the ECU 30

corrects, by feedback, the amount of fuel injection calculated as described above based on the outputs of the air-fuel ratio sensors 29a, 29b and 31, so that the air-fuel ratio of the exhaust gas from the engine becomes the stoichiometric air-fuel ratio.

Next, described below is the converter 70 according to this embodiment.

Fig. 2 is a sectional view illustrating the constitution of the converter 70 according to the embodiment. The converter 70 is of the form in which a NOx absorbing and reducing catalyst 7 is contained in a casing 70a.

The NOx absorbing and reducing catalyst 7 according to this embodiment uses a substrate of, for example, honeycomb-shaped cordierite of which the surface is coated with alumina to carry at least one component selected from alkali metals such as potassium K, sodium Na, lithium Li and cesium Cs, alkaline earth metals such as barium Ba and calcium Ca, and rare earth metals such as lanthanum La, cerium Ce and yttrium Y, as well as a noble metal such as platinum Pt. The NOx absorbing and reducing catalyst exhibits the NOx absorbing and releasing action absorbing NOx (NO₂, NO) in the exhaust gas in the form of nitric acid ions NO₃⁻ when the air-fuel ratio of the exhaust gas flowing in is lean, and releasing NOx which it has absorbed when the oxygen concentration drops in the exhaust gas flowing in.

When, for example, the engine 1 is operated at a lean air-fuel ratio and the exhaust gas of a lean air-fuel ratio flows into the NOx absorbing and reducing catalyst 7, NOx (NO) in the exhaust gas is oxidized on platinum Pt to form nitric acid ions. When, for example, BaO is used as an absorbent, the nitric acid ions are absorbed by the absorbent and diffuse in the absorbent in the form of nitric acid ions NO₃⁻ while being bonded to barium oxide BaO. In a lean atmosphere, therefore, NOx in the exhaust gas is absorbed by the NOx absorbent in

the form of a nitrate.

When the oxygen concentration sharply decreases in the exhaust gas flowing in (i.e., when the exhaust gas acquires the stoichiometric air-fuel ratio or a rich air-fuel ratio), nitric acid ions are formed in decreased amounts on platinum Pt and, hence, the reaction proceeds in the reverse direction releasing nitric acid ions NO₃⁻ in the form of NO₂ from the absorbent. Here, when the exhaust gas contains components that serve as reducing agents, such as CO, HC and H₂, then, NO₂ is reduced with these components on platinum Pt.

In this embodiment, further, a metal component such as cerium Ce is carried as an oxygen storage component on the alumina layer of the substrate to the NOx absorbing and reducing catalyst component, in order to impart the O₂ storage capability. When the exhaust gas flowing into the catalyst has an air-fuel ratio higher than the stoichiometric air-fuel ratio (when the air-fuel ratio of the exhaust gas is lean), cerium carried on the alumina layer bonds to oxygen in the exhaust gas to form ceria (cerium oxide IV: CeO₂) to store oxygen. When the air-fuel ratio of the exhaust gas flowing in is smaller than the stoichiometric air-fuel ratio (when the air-fuel ratio of the exhaust gas is rich), ceria releases oxygen and is transformed into cerium oxide III (Ce₂O₃); i.e., oxygen is released. Thus, the oxygen storage component exhibits the O₂ storage action in which the components absorb oxygen in the exhaust gas when the air-fuel ratio of the exhaust gas flowing in is lean and release oxygen into the exhaust gas when the air-fuel ratio of the exhaust gas flowing in becomes rich.

In this embodiment, when the amount of NOx absorbed by the NOx absorbing and reducing catalyst 7 increases during the lean air-fuel ratio operation of the engine 1, the rich spike operation is executed to change the engine

air-fuel ratio from a lean air-fuel ratio to a rich air-fuel ratio for a short period of time, in order to release NOx from the NOx absorbing and reducing catalyst and to purify it by reduction.

5 In this embodiment, the ECU 30 increases or decreases the value of a NOx counter to estimate the amount of NOx absorbed by the NOx absorbing and reducing catalyst 7. The amount of NOx absorbed by the NOx absorbing and reducing catalyst 7 per a unit time is proportional to the amount of NOx in the exhaust gas flowing into the NOx absorbing and reducing catalyst per a unit time, i.e., proportional to the amount of NOx emitted by the engine 1 per a unit time. On the other

15 hand, the amount of NOx emitted by the engine per a unit time is determined by the amount of fuel supplied to the engine, air-fuel ratio and flow rate of the exhaust gas. It is therefore possible to know the amount of NOx absorbed by the NOx absorbing and reducing catalyst when the engine operating conditions are determined. In this

20 embodiment, the amounts of NOx emitted by the engine per a unit time are measured in advance by changing the engine operating conditions (degree of accelerator opening, rotational speed of the engine, intake air amount, intake air pressure, air-fuel ratio, amount of fuel supplied, etc.), and the amounts of NOx absorbed by the NOx absorbing and reducing catalyst 7 per unit time are stored in the ROM in the ECU 30 in the form of a

25 numerical value map using, for example, the engine load (amount of fuel injection) and the rotational speed of the engine. The ECU 30 calculates the amount of NOx absorbed by the NOx absorbing and reducing catalyst per unit time from the engine load (amount of fuel injection) and the engine rotational speed by using the map at a regular interval (every after the above-mentioned unit time), and increases the NOx counter by the absorbed amount of NOx. Therefore, the value of the NOx counter represents the amount of NOx absorbed by the NOx

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absorbing and reducing catalyst 7 at all times. When the value of the NOx counter increases in excess of a predetermined value during the lean air-fuel ratio operation of the engine, the ECU 30 changes the operation of the engine over to a rich air-fuel ratio operation (above-mentioned mode ④ or ⑤) for a short period of time to change the air-fuel ratio of the exhaust gas from the engine over to a rich air-fuel ratio. Then, the exhaust gas of a rich air-fuel ratio flows into the NOx absorbing and reducing catalyst 7 whereby NOx that has been absorbed is released from the NOx absorbing and reducing catalyst and is purified by reduction.

10 In this embodiment, cerium, which is an oxygen-storing component, is carried in a relatively large amount by the substrate of the NOx absorbing and reducing catalyst 7 to greatly improve the NOx purification ratio when NOx is released from the NOx absorbing and reducing catalyst.

20 The reason has not been clarified yet why the oxygen storage component disposed near the NOx absorbing and reducing catalyst 7 helps improve the NOx purification ratio of the NOx absorbing and reducing catalyst, but it is thought to be as described below.

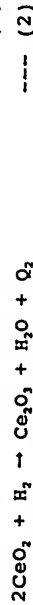
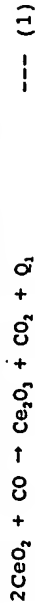
25 ① Temperature rise of the NOx absorbing and reducing catalyst due to oxygen released from the oxygen storage component.

When, for example, cerium (Ce) is carried as an oxygen-storage component by the substrate of the NOx absorbing and reducing catalyst, cerium absorbs oxygen in the exhaust gas while the engine 1 is in operation at a lean air-fuel ratio. In a state where the cerium is saturated with oxygen which it has absorbed (state where all the cerium that is carried is bonded to oxygen and is transformed into ceria (CeO_2)), the air-fuel ratio is lean to a sufficient degree near the surfaces of the NOx absorbing and reducing catalyst 7, and the NOx absorbing and reducing catalyst 7 absorbs

NOx in the exhaust gas.

After the NOx absorbing and reducing catalyst 7 has absorbed NOx in this state, the operating air-fuel ratio of the engine 1 is changed to a rich air-fuel ratio.

Then, the oxygen concentration in the exhaust gas drops, and the HC, CO and H₂ components in the exhaust gas increase. As the exhaust gas having the rich air-fuel ratio comes in contact with the ceria (CeO₂), the oxygen storage component releases oxygen which reacts with CO and H₂ components in the exhaust gas. More correctly, the following reaction takes place between the ceria and the CO and H₂ components in the exhaust gas.



The above reactions (1) and (2) are exothermic reactions generating relatively large amounts of heat Q₁ and Q₂. When the exhaust gas air-fuel ratio is changed to a rich air-fuel ratio, therefore, the ceria releases the heat in large amounts, and the temperature of the NOx absorbing and reducing catalyst disposed close thereto is rapidly raised.

As the temperature of the NOx absorbing and reducing catalyst rises, NOx absorbed by the NOx absorbent (e.g., BaO) in the form of nitric acid ions migrates at an increased rate onto the noble metal catalyst component such as Pt in the mechanism of releasing NOx from the NOx absorbing and reducing catalyst. At this moment, the noble metal catalyst component has been heated, too, and exhibits an increased catalytic activity. Accordingly, NOx that has migrated onto the noble metal catalyst component from the absorbent actively reacts with the HC, CO and H₂ components in the exhaust gas, and is reduced. That is, the rise in the temperature of the NOx absorbing and reducing catalyst promotes both the rate of releasing NOx from the NOx absorbing and reducing catalyst and the reducing reaction of NOx that is released, contributing to greatly improving the purification ratio of NOx.

As described above, the rise in the temperature of the NOx absorbing and reducing catalyst due to the reaction on the oxygen storage component takes place only when NOx is released from the NOx absorbing and reducing catalyst (i.e., when the exhaust gas air-fuel ratio is changed over to a rich air-fuel ratio) and within a very short period of time, contributing greatly to improving the purification ratio of NOx. For example, when the temperature of the NOx absorbing and reducing catalyst is raised by increasing the exhaust gas temperature or by being heated by a heater, the NOx purification ratio is not improved to a sufficient degree compared with when the oxygen storage component is disposed. It has been known that in a region higher than a given temperature, the NOx absorbing and reducing catalyst exhibits a decreased NOx absorbing capability when the air-fuel ratio is lean. The NOx absorbing capability (maximum amount of NOx absorption) of the NOx absorbing and reducing catalyst is given as a point where the rate of NOx absorbed by the absorbent (e.g., BaO) of the NOx absorbing and reducing catalyst is balanced with the rate of releasing NOx from the absorbent. Here, however, the rate of releasing NOx increases with a rise in the temperature of the absorbent. When the absorbent is heated higher than a given point, therefore, the NOx absorbing capability of the NOx absorbing and reducing catalyst decreases with a rise in the temperature. At the time of absorbing NOx (lean air-fuel ratio operation), therefore, when the temperature of the NOx absorbing and reducing catalyst is raised in excess of a given value, then, the NOx absorbing capability of the NOx absorbing and reducing catalyst drops. When NOx is being released from the NOx absorbing and reducing catalyst (rich air-fuel ratio operation), on the other hand, the NOx reducing efficiency increases with an increase in the temperature of the NOx absorbing and reducing catalyst. In order to improve the NOx reducing

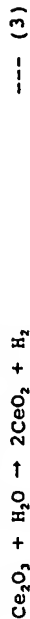
efficiency and to provide a generally high NOx purification ratio without decreasing the absorbing capability of the NOx absorbing and reducing catalyst, therefore, it becomes necessary to maintain the NOx absorbing and reducing catalyst at a relatively low temperature when NOx is being absorbed by the NOx absorbing and reducing catalyst (during the lean air-fuel ratio operation) and to maintain the NOx absorbing and reducing catalyst at a relatively high temperature when NOx is being released (during the rich air-fuel ratio operation).

Upon adjusting the temperature of the NOx absorbing and reducing catalyst by controlling the exhaust gas temperature or by the heater, however, it is not allowed to change the temperature of the NOx absorbing and reducing catalyst within a short period of time. During the lean air-fuel ratio operation, therefore, the temperature of the NOx absorbing and reducing catalyst is heated excessively resulting in a drop in the NOx absorbing capability or, during the rich air-fuel ratio operation, the temperature of the NOx absorbing and reducing catalyst is not raised to a sufficient degree and NOx is not sufficiently reduced. When the oxygen storage component is disposed close to the NOx absorbing and reducing catalyst as in this embodiment, on the other hand, the temperature of the NOx absorbing and reducing catalyst can be raised within a very short period of time when the air-fuel ratio of the exhaust gas is changed from the lean side to the rich side. During the lean air-fuel ratio operation, therefore, the NOx absorbing and reducing catalyst is maintained at a relatively low temperature to prevent a drop in the NOx absorbing capability. During the rich air-fuel ratio operation, on the other hand, the temperature of the NOx absorbing and reducing catalyst is raised within a short period of time to improve the NOx purification ratio as a whole.

② Formation of H₂ by the oxygen storage component.

Another reason why the oxygen storage component disposed near the NOx absorbing and reducing catalyst helps improve the NOx purification ratio of the NOx absorbing and reducing catalyst is thought to be that H₂ is formed by the oxygen storage component during the rich air-fuel ratio operation.

For example, the ceria (CeO₂) that is used as the oxygen storage component reacts with the H₂ and CO components in the exhaust gas as the air-fuel ratio of the exhaust gas changes from the lean side to the rich side, whereby oxygen is removed from the ceria due to the reactions represented by the above-mentioned formulas (1) and (2) and the ceria is transformed into Ce₂O₃. Under the rich air-fuel ratio condition, however, Ce₂O₃ reacts with H₂O in the exhaust gas in the direction opposite to that of the formula (2) to form H₂. That is,



H₂ is highly reductive compared to HC and CO. Therefore, when H₂ exists in the exhaust gas while NOx is being released, NOx released from the NOx absorbing and reducing catalyst is reduced highly efficiently, and the NOx purification ratio of the NOx absorbing and reducing catalyst is improved as a whole. Accordingly, the oxygen storage component disposed close to the NOx absorbing and reducing catalyst improves the purification ratio of the NOx absorbing and reducing catalyst.

As described above, the purification ratio of the NOx absorbing and reducing catalyst is improved upon disposing the oxygen storage component on the upstream side of the NOx absorbing and reducing catalyst at a position close thereto, because of either one or both of the above-mentioned reasons ① and ②.

In this embodiment, the NOx absorbing and reducing catalyst component and the oxygen storage component are carried in a state of being isolated in the form of layers as will be described below. Fig. 3 is a sectional view schematically

illustrating the state of carrying the NOx absorbing and reducing catalyst component and the oxygen storage component according to this embodiment.

According to this embodiment as shown in Fig. 3, the so-called two-layer-coated structure is employed in which a NOx absorbing and reducing catalyst layer 73 is formed on the substrate 71 and, an oxygen storage component layer 75 is formed on the NOx absorbing and reducing catalyst layer 73. The exhaust gas, first, passes through the porous oxygen storage component layer 75 and, then, reaches the NOx absorbing and reducing catalyst layer 73 of the lower side. In this case, the oxygen storage component is disposed on the upstream side of the NOx absorbing and reducing catalyst component close thereto.

In this embodiment, the honeycomb-shaped cordierite or the like material is used as the substrate 71, which is then coated with alumina to carry the above-mentioned NOx absorbing and reducing catalyst components (e.g., noble metal components such as Pt, Rh, etc. and NOx absorbent such as barium Ba) thereby to form the NOx absorbing and reducing catalyst layer 73.

The oxygen storage component layer 75 is obtained by forming a porous layer of such as zeolite on the upper side (outer side) of the alumina coating and carrying noble metals and oxygen storage components on this layer. In this embodiment, among the zeolite-type materials, mordenite is used as a carrying layer for the oxygen storage component layer 75, and platinum Pt, which

is a noble metal, and cerium Ce, which is an oxygen storage component, are carried by the mordenite layer.

The thickness of the oxygen storage component layer 75 is smaller than the thickness of the NOx absorbing and reducing catalyst layer 73, i.e., about 1/6 to about 1/5 of the thickness of the NOx absorbing and reducing catalyst layer 73.

Described below is the effect of when the oxygen storage component layer 75 and the NOx absorbing and reducing catalyst layer 73 are arranged as a two-layer-coated structure as contemplated in this embodiment.

In this embodiment, heat is generated by the NOx absorbing and reducing catalyst layer 73, and H₂ is formed by the oxygen storage component layer when NOx is being released. In this embodiment in which the oxygen storage component layer 75 and the NOx absorbing and reducing catalyst layer 73 are arranged as a two-layer-coated structure, the whole NOx absorbing and reducing catalyst layer is uniformly and intimately adhered to the oxygen storage component layer enabling the temperature of the NOx absorbing and reducing catalyst to be raised more efficiently and H₂ to be supplied more efficiently by the oxygen storage component layer.

Upon forming the zeolite (mordenite in this embodiment) layer on the NOx absorbing and reducing catalyst layer 73 to carry a noble metal (Pt in this embodiment) according to this embodiment, there can be obtained a further effect.

The exhaust gas from the internal combustion engine contains sulfur oxide (SOx) formed by the burning of a sulfur component contained in the lubricating oil and fuel. SOx in the exhaust gas is absorbed by the NOx absorbing and reducing catalyst to form sulfate (e.g., BaSO₄) in the absorbent in accordance with the same mechanism as that of absorbing NOx under the lean air-

fuel ratio condition. However, the sulfate formed in the
absorbent is stable compared to nitrate, and is not
released under the condition in which NOx is released
from the NOx absorbing and reducing catalyst but
gradually builds up in the NOx absorbing and reducing
catalyst. As SOx builds up in increased amounts in the
absorbent in the NOx absorbing and reducing catalyst, the
amount of the absorbent that can take part in the
absorption of NOx decreases, and the NOx absorbing
capability (maximum amount of NOx absorption) of the NOx
absorbing and reducing catalyst decreases, i.e., a so-
called SOx contamination occurs. Upon forming the
zeolite layer on the NOx absorbing and reducing catalyst
layer according to this embodiment, SOx in the exhaust
gas is adsorbed by the zeolite as the exhaust gas passes
through the porous layer, and virtually no SOx is
contained in the exhaust gas arriving at the NOx
absorbing and reducing catalyst layer 73. Therefore, the
SOx contamination of the NOx absorbing and reducing
catalyst does not occur. Besides, SOx is adsorbed by the
zeolite without forming sulfate such as BaSO₄ in the
manner similar to that of physical adsorption.
Therefore, SOx is easily desorbed under the normal
condition where NOx is released from the NOx absorbing
and reducing catalyst. SOx that is desorbed is released
into the exhaust gas without coming in contact with the
lower NOx absorbing and reducing catalyst layer 73 and is
not absorbed by the NOx absorbing and reducing catalyst.
That is, in this embodiment, the oxygen storage component
layer 75 formed on the NOx absorbing and reducing
catalyst layer 73 also works as an SOx trap to easily
adsorb and desorb SOx. In this embodiment in which noble
metal components such as Pt and the like are carried by
the zeolite layer, further, SO₂ in the exhaust gas is
oxidized and is converted into SO₃ as it passes through
the zeolite layer. SO₃ is more easily adsorbed by the
zeolite than SO₂ and is easily desorbed from the zeolite

at a relatively low temperature (e.g., about 300°C) in a
rich air-fuel ratio atmosphere. In this embodiment,
therefore, the oxygen storage component layer 75 exhibits
further improved performance as the SOx trap.

In this embodiment, the oxygen storage
component layer is formed over the full length of the
substrate of the NOx absorbing and reducing catalyst. As
described earlier, however, the amount of NOx absorbed by
the NOx absorbing and reducing catalyst tends to increase
in the upstream half portion of the substrate. The
two-layer-coated structure may, in other embodiments, be
formed in the upstream half portion of the substrate only,
and the oxygen storage component layer may be formed in the upstream half portion only of
the substrate.

Next, described below are the carried amounts
of the oxygen storage components in the cases of Figs. 1,
2 and 3. As described above, the oxygen storage
components are disposed on the upstream side of the NOx
absorbing and reducing catalyst close thereto to improve
the NOx purification ratio of the NOx absorbing and
reducing catalyst. In order to maximize the NOx
purification ratio, however, the carried amount of the
oxygen storage component must be adjusted to lie within
an optimum range. When the oxygen storage component is
carried in too small an amount, for example, heat is
generated in a small amount by the reaction of the H₂ and
CO components with the oxygen storage component when the
air-fuel ratio of the exhaust gas becomes rich and,
hence, the temperature of the NOx absorbing and reducing
catalyst components is not raised to a sufficient degree.
When the oxygen storage component is carried in too large
an amount, on the other hand, heat is generated in
sufficiently large amounts by the reaction. However, in
this case, a large portion of the H₂ and CO components in
the exhaust gas are oxidized by the oxygen storage
component on the upstream side, and the reducing

components are not supplied in a sufficient amount to the NOx absorbing and reducing catalyst so that the released NOx is not reduced to a sufficient degree.

Fig. 4 is a graph illustrating the measured results of a change in the NOx purification ratio of the NOx absorbing and reducing catalyst as a whole while changing the amount of the oxygen storage component (cerium) carried by a portion of the NOx absorbing and reducing catalyst of the upper

layer side in the embodiment of Figs. 2 and 3.

Fig. 4 illustrates the case where the cerium as an oxygen storage component is carried in the form of a ceria-zirconia solid solution (CeO_2 and ZrO_2 at a molar ratio of 1 to 1). It has been found that the NOx purification ratio of the NOx absorbing and reducing catalyst as a whole is most improved when the ceria-zirconia solid solution is carried in an amount within a range of from 30 grams/liter to 50 grams/liter.

CLAIMS

1. An exhaust gas purification device for an internal combustion engine, comprising a NOx absorbing and reducing catalyst which absorbs NOx in the exhaust gas when the air-fuel ratio of the exhaust gas flowing in is lean and releases the absorbed NOx and purifies it by reduction when the air-fuel ratio of the exhaust gas flowing in is rich, disposed in an exhaust passage of the internal combustion engine which is capable of selecting, as required, the operation at a lean air-fuel ratio and the operation at a rich air-fuel ratio, so that the NOx absorbing and reducing catalyst absorbs NOx in the exhaust gas when the engine is operated at a lean air-fuel ratio and that the absorbed NOx is released from the NOx absorbing and reducing catalyst and is purified by reduction when the engine is operated at a rich air-fuel ratio;

wherein said NOx absorbing and reducing catalyst includes a substrate, a NOx absorbing and reducing catalyst layer carrying NOx absorbing and reducing catalyst components on said substrate, and an oxygen storage component layer carrying oxygen storage components which absorb oxygen in the exhaust gas when the air-fuel ratio of the exhaust gas is lean and release the absorbed oxygen when the air-fuel ratio of the exhaust gas is rich, said oxygen storage component layer being formed on said NOx absorbing and reducing catalyst layer.

2. An exhaust gas purification device for an internal combustion engine according to Claim 1, wherein said oxygen storage component layer comprises a zeolite layer carrying a noble metal component and a cerium component as an oxygen storage component.

3. An exhaust gas purification device for an internal combustion engine according to Claim 2, wherein said cerium is carried in the form of a ceria-zirconia solid solution, and the amount of said solid solution carried by said oxygen storage

component layer is in a range of from 30 grams/litre to 50 grams/litre.

4. An exhaust gas purification device for an internal combustion engine according to Claim 1, wherein the oxygen storage component in the upstream half portion of the substrate of said NOx absorbing and reducing catalyst is cerium carried in the form of a ceria-zirconia solid solution, and the carried amount of said solid solution is in a range of from 30 grams/litre to 50 grams/litre.

5. An exhaust gas purification device substantially as hereinbefore described with reference to the accompanying drawings.

Application No: GB 0023929.3
Claims searched: 1-5

Examiner: Dr Albert Mthupha
Date of search: 26 February 2001

Patents Act 1977 Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.S): B1W (WAX, WD, WX)

Int CI (Ed.7): B01D (53/94); F01N (3/08, 3/10, 3/18, 3/20, 3/24, 3/28, 3/36)

Other: EPODOC, JAPIO, WPI.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	EP 0885657 A2 1. ENGELHARD, see whole document, note Example	1
Y	WO 97/23278 A1 ENGELHARD, see whole document, note page 15 lines 4-20, page 28 line 35-page 30 line 6.	1
Y	US 5473887 A TOYOTA, see whole document.	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
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